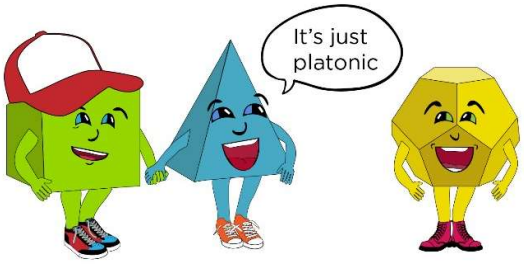
3. This question is about cubane

Platonic solids are three-dimensional shapes where all faces, edges, and angles are congruent (identical). There are only five such solids. Plato hypothesised that the classical elements — air, earth, fire, and water — each corresponded to one of the shapes.



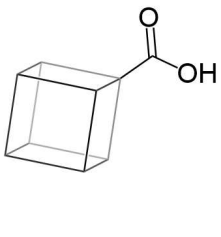
With the advances in chemistry in the last 2360 years, we no longer think that there are four elements or that they are made of Platonic solids. However, we can make a Platonic solid out of elements.

One such molecule, cubane, is of interest and potential use because of its unusual structure.

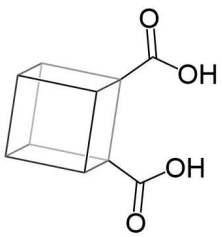
Skeletal formula of cubane

(a) State the molecular formula of cubane.

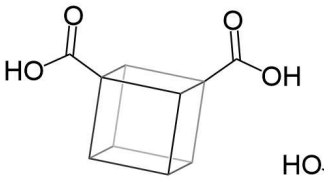
One synthesis of cubane proceeds via cubane-1,4-dicarboxylic acid. The structures of cubane-carboxylic acid and the three isomers of cubane-dicarboxylic acid are shown below.



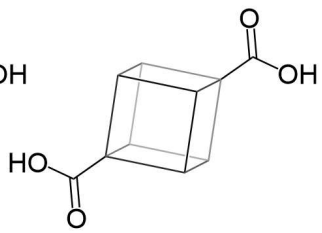
Cubane-carboxylic acid



Cubane-1,2-dicarboxylic acid



Cubane-1,3-dicarboxylic acid



Cubane-1,4-dicarboxylic acid

(b) Complete the table in the answer booklet with the number of peaks in the ^{13}C NMR spectrum of:

(i) Cubane

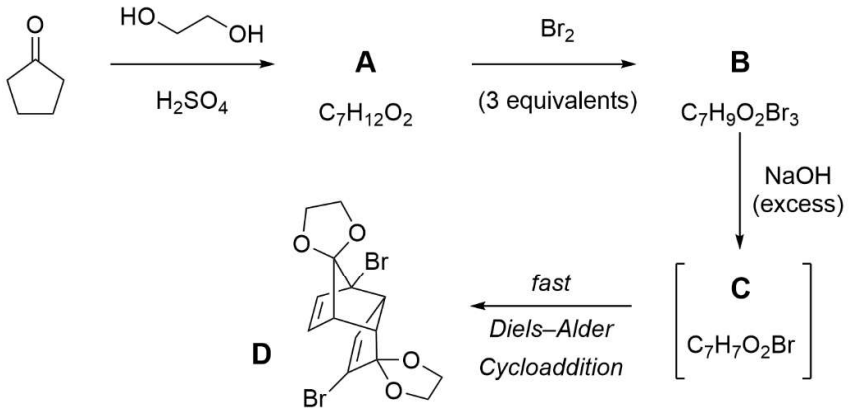
(ii) Cubane-carboxylic acid

(iii) Cubane-1,2-dicarboxylic acid

(iv) Cubane-1,3-dicarboxylic acid

(v) Cubane-1,4-dicarboxylic acid.

The start of the cubane synthesis is shown below.



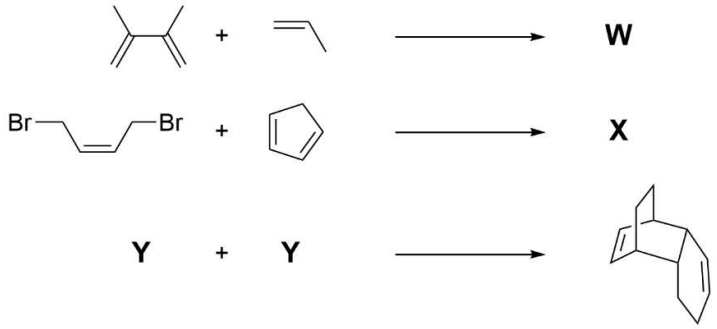
A was treated with three equivalents of Br_2 to form **B**. In **B**, which has the molecular formula $C_7H_9O_2Br_3$, each of the three bromine atoms are exactly **three bonds away** from the two oxygen atoms.

B was then reacted with excess sodium hydroxide. This reaction is proposed to proceed via intermediate **C**, which then reacts with another molecule of itself to form compound **D**.

(c) Draw the structures of **A** and **B**.

The reaction from intermediate **C** to **D** is known as a Diels-Alder cycloaddition. The simplest example of a Diels-Alder cycloaddition, between butadiene and ethene, is shown on the right.

Three other examples of Diels–Alder cycloadditions are shown below:

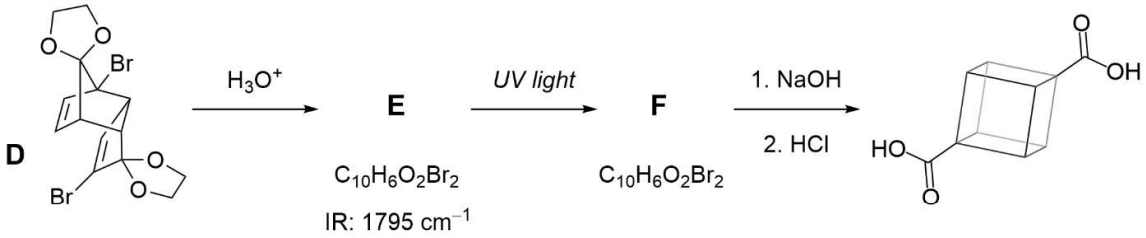


(d) Draw the structures of products **W** and **X**.

Y dimerises via a Diels-Alder reaction to produce the product shown.

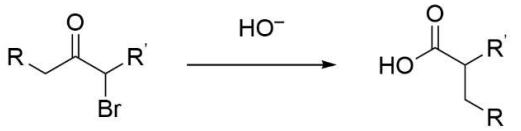
(e) Draw the structure of starting material **Y**.

(f) Based on this knowledge of the Diels-Alder reaction, draw the structure of intermediate **C**.



Compound **D** reacts with aqueous acid to form compound **E**, which on exposure to UV light, reacts **intra**molecularly to form compound **F**. Compound **F** contains two four-membered rings.

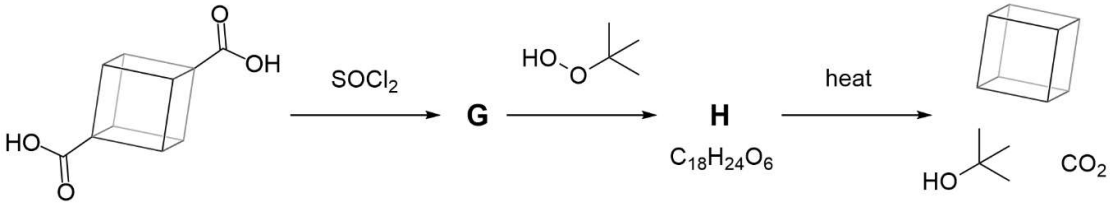
Lastly, compound **F** is reacted with sodium hydroxide followed by hydrochloric acid. This results in a reaction known as the Favorskii Rearrangement. The general reaction for a Favorskii Rearrangement is shown here:



(g) On the structure in the answer booklet, circle the electrophilic carbon atom(s).

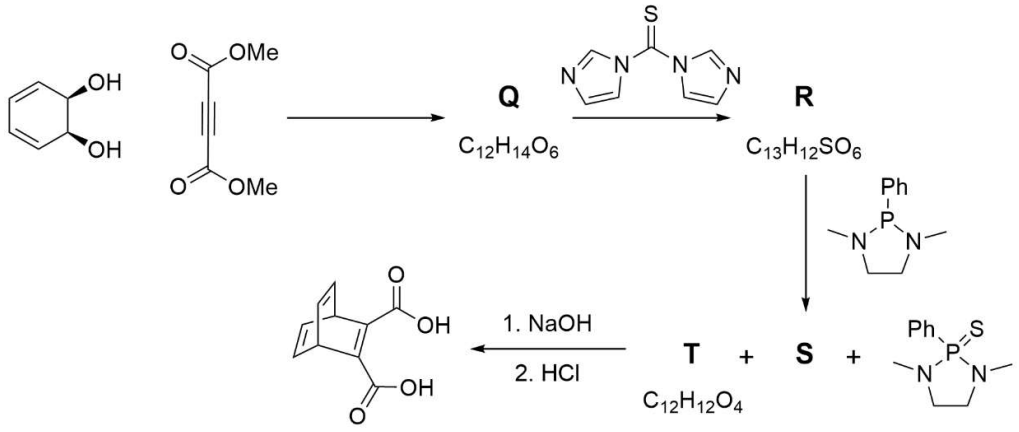
(h) Using the frameworks provided in the answer booklet, draw the structures of **E** and **F**.

This dicarboxylic acid can be chemically converted to cubane.



(i) Using the frameworks provided in the answer booklet, draw the structures of **G** and **H**.

An isomer of cubane, barrelene, can also be constructed using a Diels-Alder reaction.



The two starting materials undergo a Diels-Alder reaction to form **Q**. An additional ring is formed to give product **R**, which then reacts to give three products, one of which is shown. Compound **S** is a gas, and compound **T** when treated with NaOH gives barrelene-1,2-dicarboxylic acid.

(j) Using the frameworks provided in the answer booklet, draw the structures of **Q**, **R**, **S**, and **T**.